

# Synthesis of Stilbene by the Wittig and Horner-Wadsworth-Emmons Reactions

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Part A (p. 606)(p.590 4<sup>th</sup> ed.) - Wittig reaction for the synthesis of stilbene.

Part B (p. 610)(p.594 4<sup>th</sup> ed.) - Wadsworth-Emmons reaction for the synthesis of stilbene.

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## Important Concepts

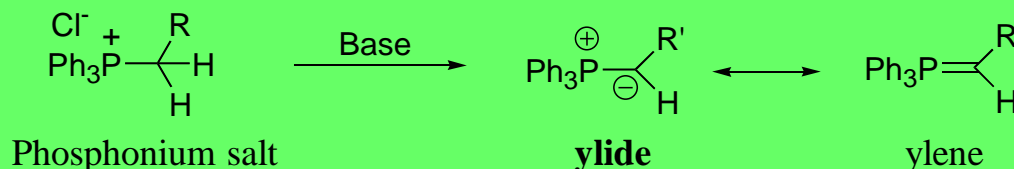
- Synthetic methods for making double bonds (olefins)
  - Phosphonium salt, ylide, phosphonate ester
  - Transition state controls Wittig stereochemistry (cis)
- Ring closure controls Wadsworth-Emmons stereochemistry (trans)
  - cis-trans photoisomerization with iodine

# The Wittig Reaction

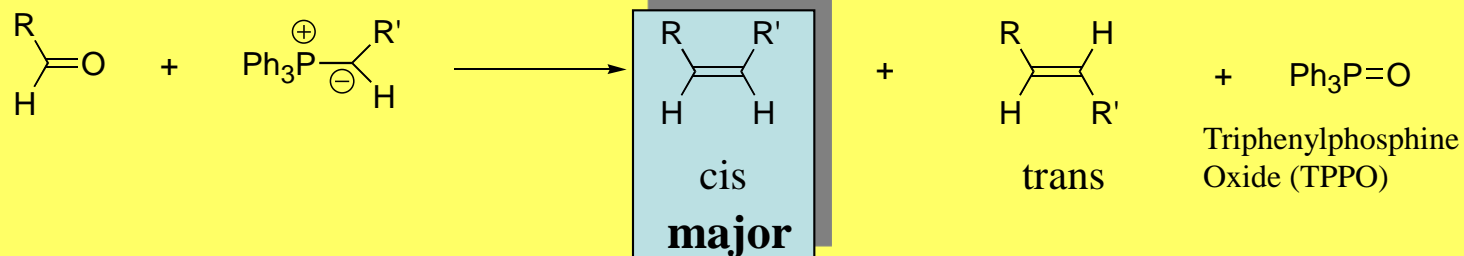


**Georg Wittig** (1897 - 1987)  
Born in Berlin Germany  
University of Heidelberg  
Nobel Prize - 1979

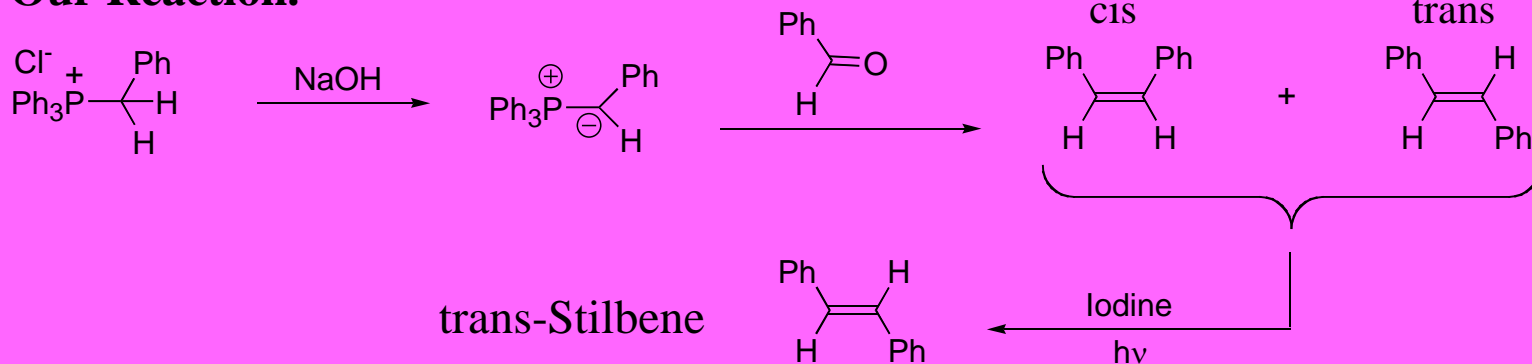
## Step 1 - Formation of the ylide.



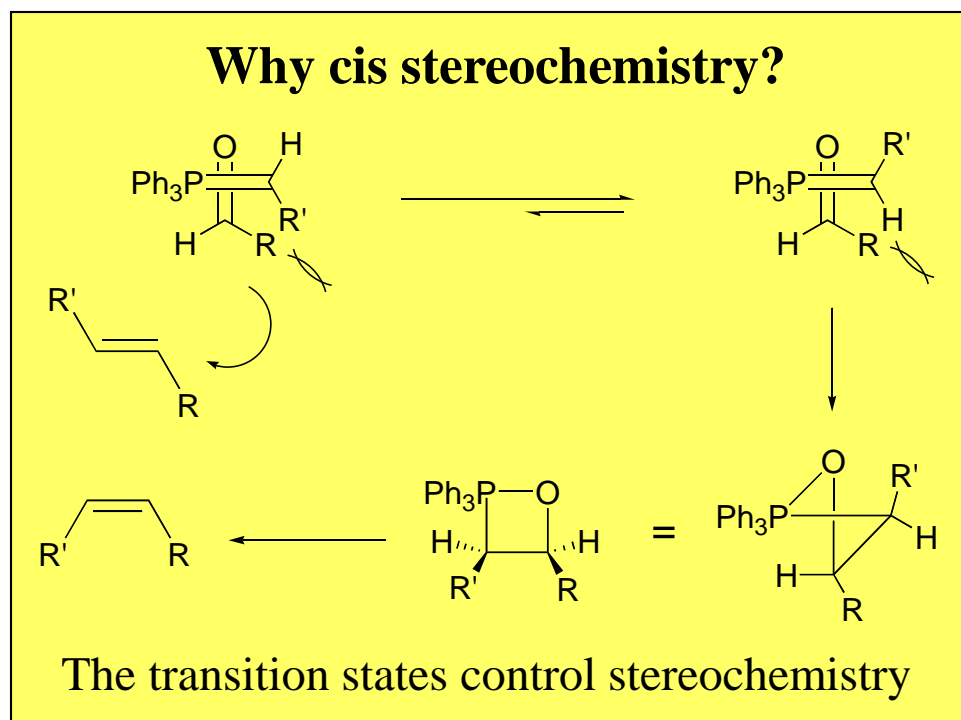
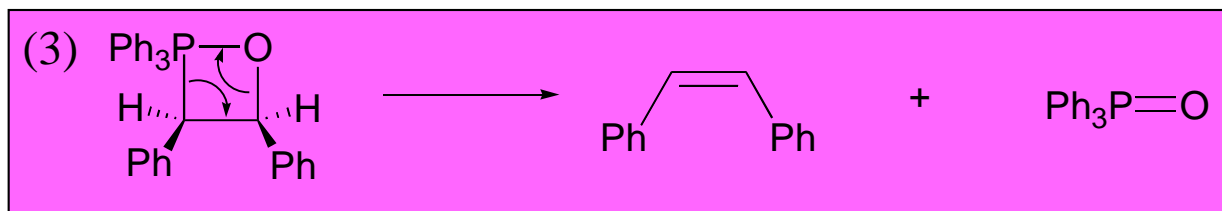
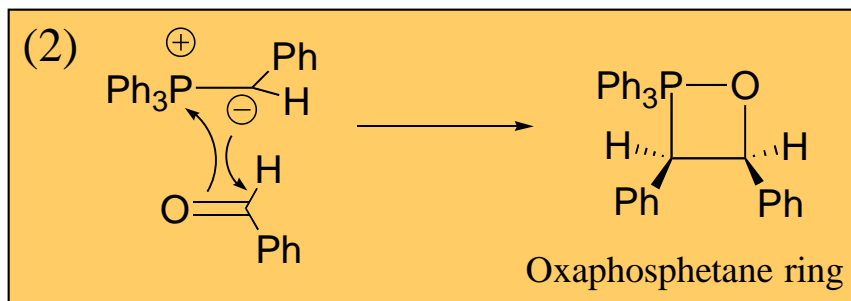
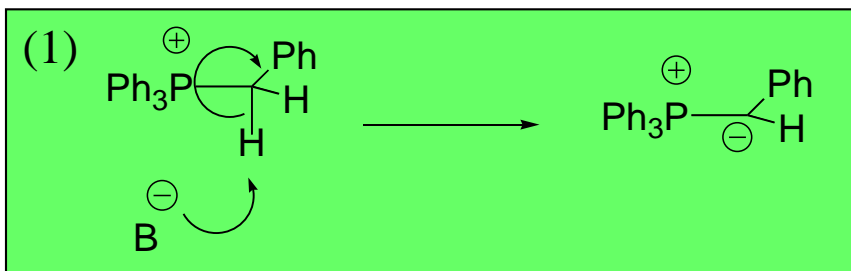
## Step 2 - Addition to the carbonyl (aldehyde or ketone).



## Our Reaction.



# The Wittig Reaction Mechanism

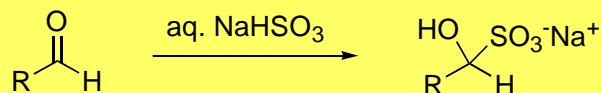


# Procedural Details - Wittig

## Week 1

- For the Wittig reaction follow the procedure in the book.
- Do not evaporate solvent after initial workup.
- Save a small amount of crude for TLC analysis.
- Add iodine to flask and stopper with a rubber septum. Label flask and place in hood, with light on, until next week.

### Why wash with aq. NaHSO<sub>3</sub>?



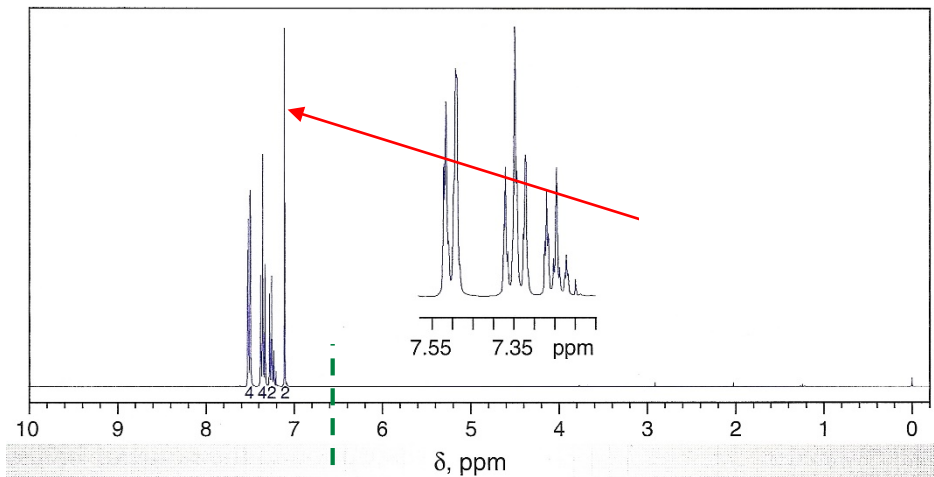
### Why wash with aq. NaCl?

- to remove water from solvent

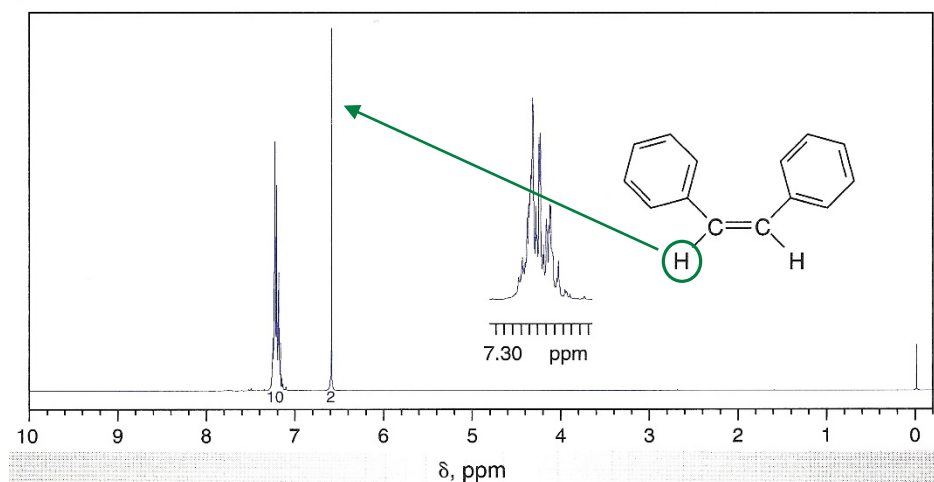
## Week 2

- Add solvent if necessary and follow workup procedure.
- Recrystallize once from 95% ethanol. There is no need to recrystallize a second time.
- No Bromine or Bayer tests for unsaturation.
- Get TLC of cis/trans, plus final Wittig and Wadsworth-Emmons products on same plate.
- Get data from Wadsworth-Emmons and include in your report (e.g. as if you had performed both reactions). The procedure section should only have your reaction, not your partners.

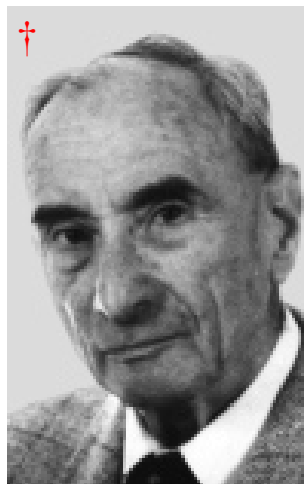
# Determining the cis/trans ratio from NMR spectra



Integrate the vinylic protons to determine the cis:trans ratio



# The Horner-Wadsworth-Emmons Reaction

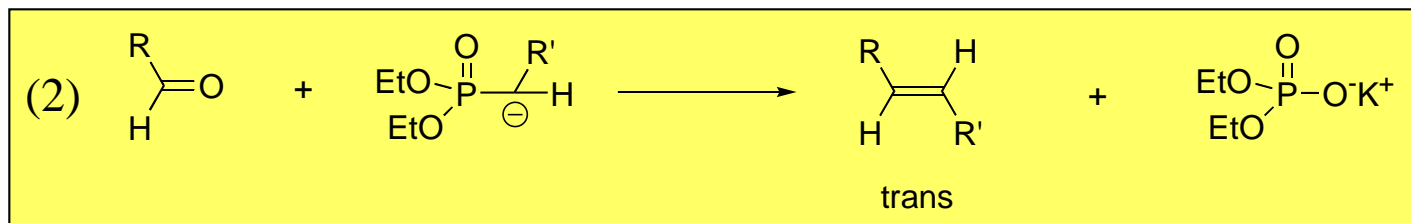
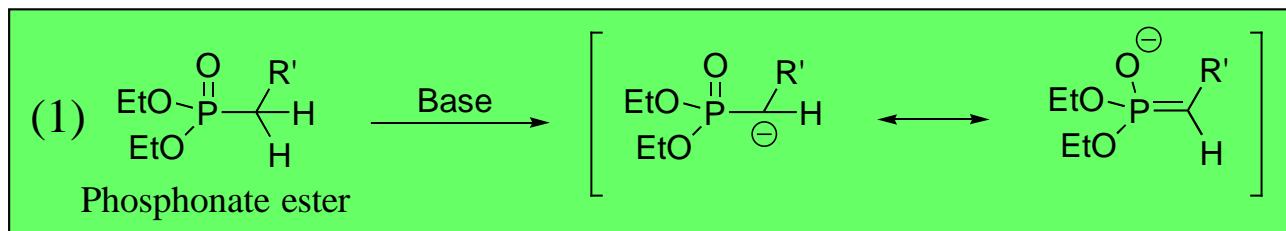


**Leopold Horner** (1911 - 2005)  
Born in Kehl am Rhein Germany  
University of Mainz

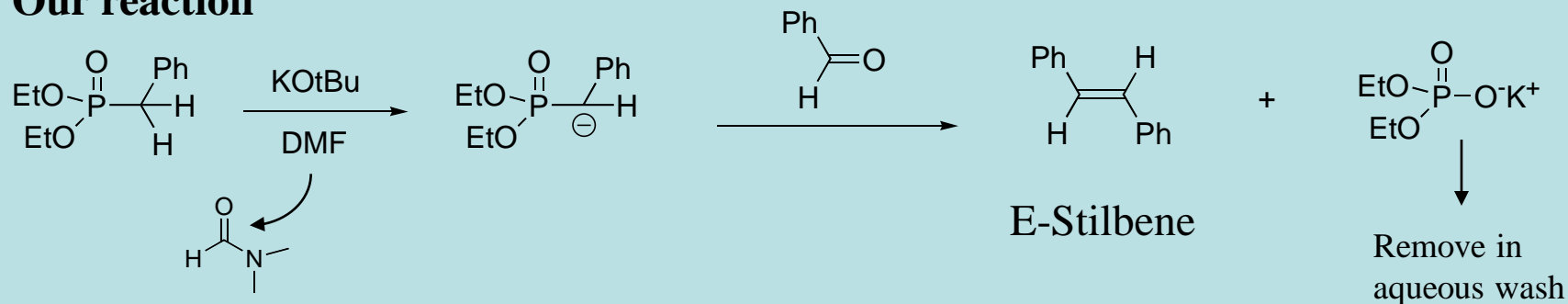
**William S. Wadsworth &**

**William D. Emmons** (1924 - 2001)

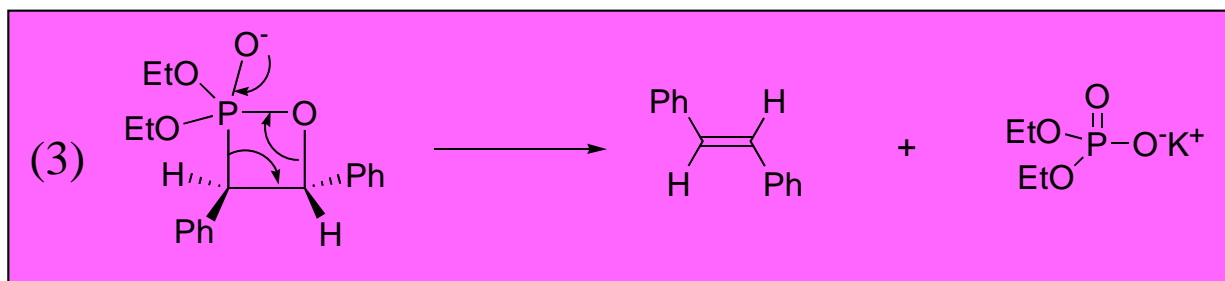
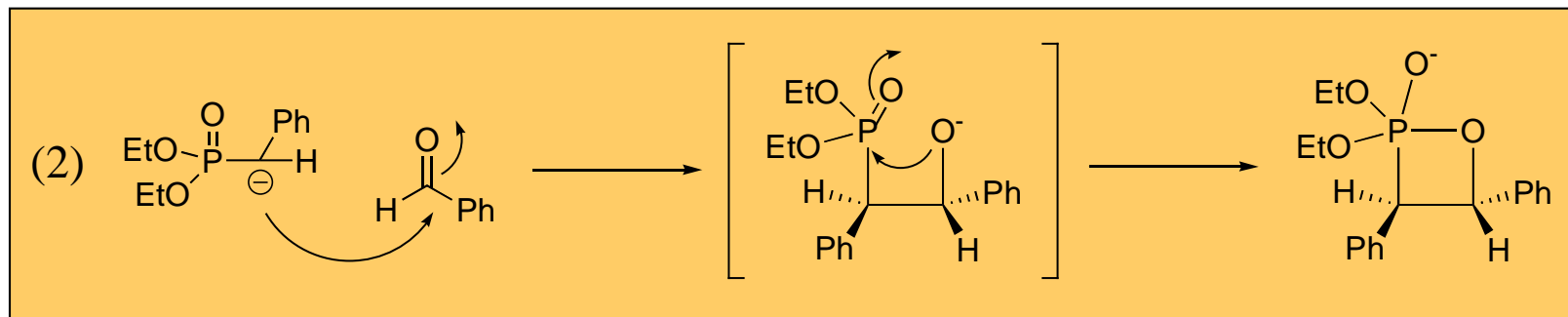
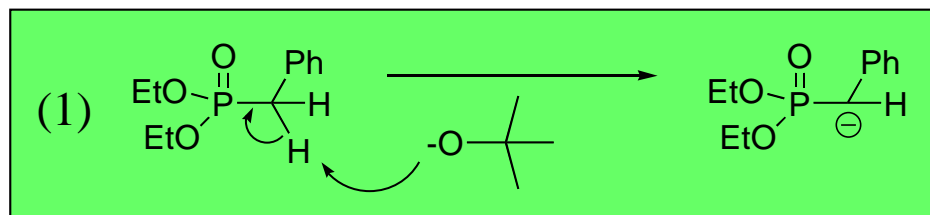
Born in Minnesota, BS - U. MN, Ph.D. - U. IL  
Rohm & Haas



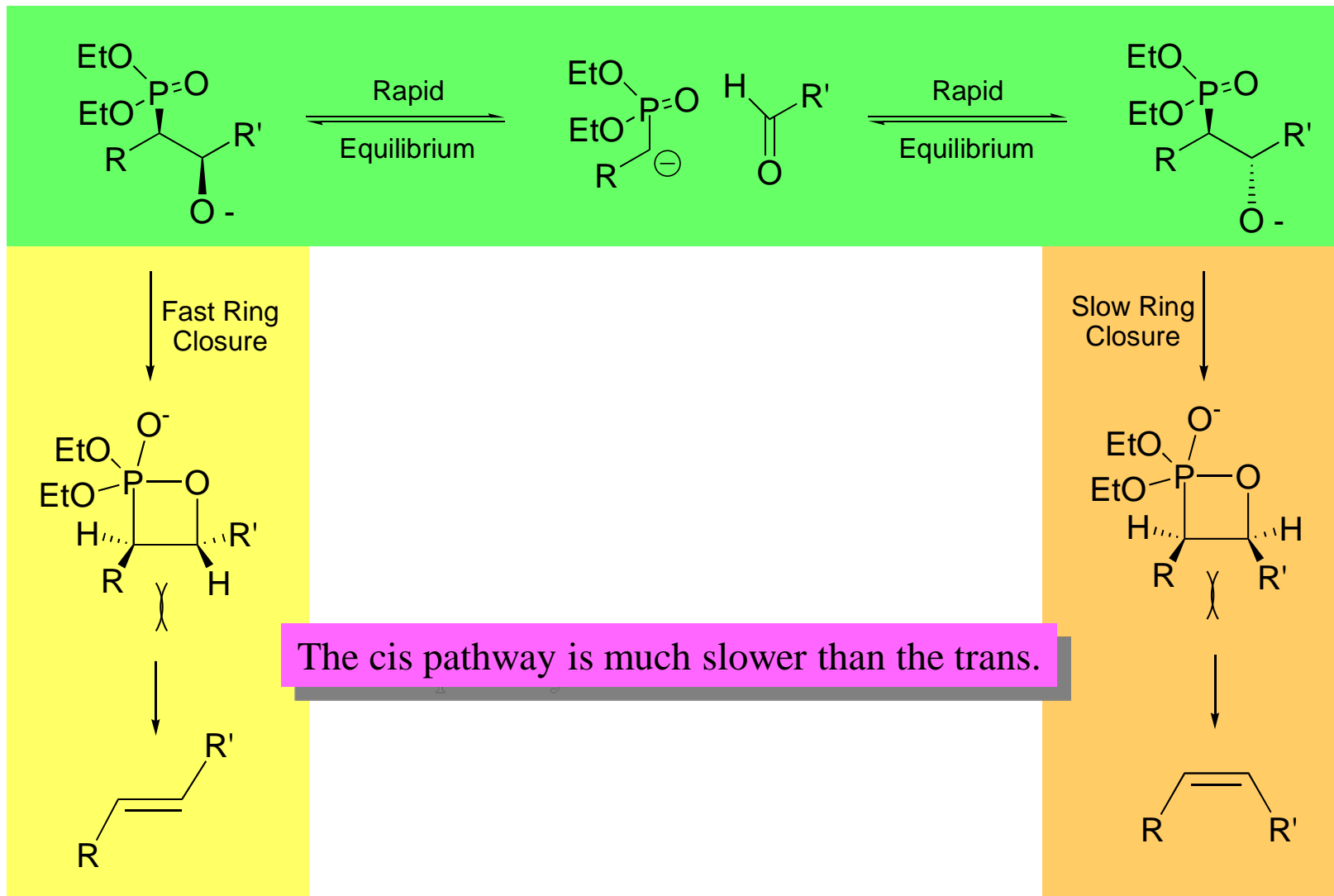
## Our reaction



# The Horner-Wadsworth-Emmons Reaction Mechanism



# Why is the trans Product Favored for Horner-Wadsworth-Emmons?



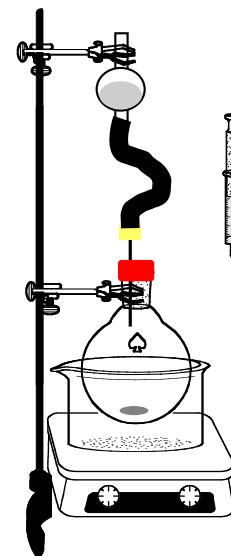


# Procedural Details - Wadsworth-Emmons

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## Week 1

- Put a stir bar in the 25 ml RB flask and place in oven at beginning of class for 20 minutes and let it cool in the dessicator cabinet. No flame or heat-gun is required for drying.
- Place a rubber septum over the RB flask immediately after removing from dessicator cabinet.
- Assemble apparatus with  $\text{CaCl}_2$  drying tube connected to needle, which penetrates rubber septum.
- Use a plastic syringe to add reagents through the septum.
- *Be very careful with the needles.*
- After workup you do not need to save any of the crude for NMR analysis.
- Recrystallize from 95% ethanol.



## Week 2

- Get data from Wittig and include in your report (e.g. as if you had performed both reactions). The procedure section should only have your reaction, not your partners.

# Required Data

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## Wittig

- m.p. of purified product.
- TLC with crude, pure Wittig and pure Wadsworth-Emmons on same plate.
- Weight, % Yield
- IR and  $^1\text{H}$  NMR of starting materials and final product.
- $^1\text{H}$  NMR of crude cis/trans mixture.

## Horner-Wadsworth-Emmons

- m.p. of purified product.
- TLC with crude, pure Wittig and pure Wadsworth-Emmons on same plate.
- Weight, % Yield
- IR and  $^1\text{H}$  NMR of starting materials and final product.

# Photoisomerization with Iodine

